

4. OPERATIONAL PLAN FOR THE PHASE II

DRI will investigate more detailed time-resolved measurements to test the hypothesized relationship between emissions sources and the diurnal and day-of-the-week variations in key primary pollutants, NMHC/NO_x and NO₂/NO_x ratios. The field measurements will involve two approaches: supplemental measurements at existing SCAQMD monitoring sites and mobile sampling during periods that coincide with overnight carryover of O₃ precursors, O₃ inhibition, and O₃ accumulation. The measurements will be used to attribute weekday-weekend changes in the temporal and spatial patterns of VOC and NO concentrations to major sources of ozone precursor emissions. While exhaust emissions from on-road gasoline and diesel vehicles are the primary sources of interest, detailed speciation of VOC will also allow for source attribution of other sources of VOC. Supplemental measurements will be made during a two-week period in late September to early October 2000.

4.1 Supplemental Measurements at SCAQMD Monitoring Stations

The existing network of continuous O₃, NO/NO_x, CO, and PM₁₀ mass will serve as a foundation for the measurement program. Data for speciated hydrocarbon and carbonyl compounds are collected at seven Photochemical Assessment Monitoring Stations (PAMS) within SoCAB. PAMS precursor monitoring is conducted annually in the SoCAB from July 1 to September 30. Table 4-1 shows the locations and sampling schedule and Table 4-2 show the list of PAMS target compounds. Hydrocarbon measurements include eight, 3-hour samples daily at Pico Rivera and Burbank, and eight 3-hour samples every third day at Hawthorne, Azusa and Upland, Banning and Santa Clarita. Carbonyl compounds are measured at Burbank, Pico Rivera and Banning (eight 3-hour samples every day). Other data include PAMS-type measurements by ARB at Los Angeles – N. Main (four 3-hour canister samples every third day). Of the available PAMS VOC sampling, the daily measurements at Pico Rivera and Burbank will be useful for our short-term field study. We will add hourly speciated VOC measurements at Azusa by automated gas chromatography with ion trap mass spectrometry (auto-GC/MS). In addition, concentrations of black carbon will be estimated at both Pico Rivera and Azusa by light absorption using aethalometers. DRI personnel will install, calibrate and maintain the supplemental instruments during the two-week deployment.

The auto-GC/MS is currently being used in the Central California Ozone Study (CCOS) through September 17, 2000. The instrument will be installed at Azusa on 9/26/00 and operated from 9/27/00 to 10/8/00. We will explore the possibility of having SCAQMD continue the operation of their auto-GC at Pico Rivera until 10/8/00.

4.2 Mobile Monitoring

Primary pollutants (CO, NO, black carbon [BC] and speciated hydrocarbons) will be monitored simultaneously in a mobile van along several freeway loops in different area of the basin from downtown Los Angeles to San Bernardino. Carbon monoxide (TEI 48), NO/NO_y¹

¹ Reactive oxidized nitrogen (NO_y) include nitric oxide (NO), nitrogen dioxide (NO₂), peroxyacetylnitrate (PAN) and other PAN analogues, nitric acid (HNO₃), nitrate aerosol (NO₃⁻), nitrous acid (HONO), peroxyntic acid (HNO₄), nitrate radical (NO₃[•]), dinitrogen pentoxide (N₂O₅), and organic nitrates (ORNI).

(TEI 42S) and black carbon estimated from light absorption (Anderson RTAA-1000 aethalometer) will be measured continuously with averaging times of 1, 1, and 5 minutes, respectively. Canister and Tenax cartridge samples will be integrated over a period of 50 minutes for each freeway loop (see below). Canisters will be analyzed in the laboratory for CO, CO₂, methane, MTBE, and C₂-C₁₁ hydrocarbons, and C₈-C₁₈ hydrocarbons will be quantified from Tenax samples. The mobile sampling data will be used to characterize the diurnal variations in relative contributions of gasoline and diesel vehicles to ambient level of ozone precursors by day of the week.

Mobile sampling will be conducted during the carryover period between 2-5 a.m. (PDT), and the morning commute period between 6 to 9 a.m. along the following highway loops.

- Los Angeles Loop: South on I-5/10 from I-10/US-101 (Hollywood Freeway), west on I-10, north on S110, south on I-5 (loop distance ~ 12 miles)
- Pico Rivera Loop: South on I-605 from I-10, northwest on I-5, north on I-710, east on I-10 (loop distance ~ 26 miles)
- West Covina Loop: east on I-10 from I-605, south on S-57, west on S-60 (Pomona Freeway), north on I-605, (loop distance ~ 22 miles).

Sampling during the carryover period will begin with the West Covina loop and end with the Los Angeles loop. Order will be reversed during the commute period with West Covina being the last sampling loop. Measurements will also be made during the ozone accumulation period between 10 a.m. to noon along the following freeway loops covering central and eastern portions of the basin.

- Pomona/Ontario Loop: east on I-10 from S-57 (Orange Freeway), south on I-15, west on S-60, north on S-57 (loop distance ~25 miles).
- Riverside/San Bernardino Loop: east on I-10 at I-15, south on I-215, west on S-60, and north on I-15 (loop distance ~23 miles).

Mobile sampling will be conducted over a nine-day period beginning on Saturday, 9/30/00 and ending on Sunday, 10/8/00. Sampling will be conducted on two Saturdays, two Sundays, one Monday, one Wednesday, and one Friday.

For each loop, the time series of NO and CO will be related to indicators of compression-ignition exhaust (black carbon and heavy hydrocarbon) and spark-ignition exhaust (MTBE) for the carryover, ozone inhibition, and ozone accumulation period by day of the week. From the [NO], [CO], [BC], [MTBE], and [nC₁₀-nC₁₅], we will estimate the fraction contributions of spark-ignition and compression-ignition emissions of NO, and NMHC as described below.

First, we will use [BC]/[MTBE] ratios to estimate the ratio of vehicle miles traveled by compression-ignition vehicles to spark-ignition vehicle (VMTci/VMTsi) using the following equation.

$$\frac{[BC]}{[MTBE]} = \frac{BCci}{MTBEsi} \times \frac{VMTci}{VMTsi}$$

where

[BC] = measured black carbon concentration in µg/m³,

[MTBE] = measured MTBE concentrations in µg/m³,

BCci = assumed average CI emission rate of black carbon in grams/mile, and

MTBEsi = assumed average SI emission rate of MTBE in grams/mile.

$$\text{The ratio of VMT, } A = \frac{VMTci}{VMTsi} = \frac{[BC]}{[MTBE]} \times \frac{MTBEsi}{BCci}$$

Ratio of the CI and SI source contribution estimates (sce) to NO can be estimated from *A* and assumed average NO emission rates for CI and SI as follows.

$$\frac{NOsceci}{NOscesi} = \frac{NOci}{NOsi} \times A$$

Ratios of the CI and SI source contribution estimates to NMHC and CO can be estimated in the same way.

The ratio of VMT due to CI and VMT due to SI, *A*, can also be estimated from [CO] and [NO].

[CO] is proportional to $COci \times VMTci + COsi \times VMTsi$ and

[NO] is proportional to $NOci \times VMTci + NOsi \times VMTsi$

where

[CO] = measured carbon monoxide concentration in µg/m³,

[NO] = measured nitric oxide concentrations in µg/m³,

COci and COsi = assumed average CI and SI emission rates of CO in grams/mile, and

NOci and NOsi = assumed average CI and SI emission rates of NO in grams/mile.

A is determined from the following equation.

$$\frac{[CO]}{[NO]} = \frac{COciA + COsi}{NOciA + NOsi}$$

4.3 Measurement Methods

This section describes the methods that will be used to carry out the measurements that are proposed in Sections 4.1 and 4.2.

4.3.1 Aethalometer

Light absorbing aerosol (e.g., black carbon) deposited on a filter can be quantified through the measurement of light transmission or reflection. A real-time version of the integrating plate method, the aethalometer (Hansen et al., 1984), continuously collects aerosol on a quartz-fiber filter tape. During the deposition process, the light attenuation through the aerosol collection spot and an unloaded reference spot are monitored. Their difference yields the absorption due to the integral of all light-absorbing materials collected on a particular spot. The time derivative of this quantity is a measure of the current aerosol light absorption. When the optical density of the aerosol spot reaches a certain value, the filter tape advances automatically. Time resolution available with the aethalometer varies from seconds or minutes in urban areas to ten minutes in rural locations and longer in very remote locations. One filter tape is sufficient for approximately 700 aerosol collection spots corresponding to one or more months of operation in urban areas, a year or more in rural areas.

The aethalometer converts the result of its filter attenuation measurement into BC mass concentration by a conversion factor of 19.2 m²/g. Aethalometer BC agrees with collocated filter samples analyzed for elemental carbon.(Hansen and McMurry, 1990). Applications of the aethalometer include air quality monitoring in urban(Hansen and Novakov, 1989; Hansen and Novakov, 1990) and more remote locations,(Rosen et al., 1984; Hansen et al., 1993; Pirogov et al., 1994) transport studies,(Parungo et al., 1994) and source characterization.(Hansen and Rosen, 1990).

4.3.2 NO and NOy

Nitric oxide (NO) is continuously measured by the chemiluminescence nitric oxide-ozone method. This method is based on the gas-phase chemical reaction of NO with ozone. In this method an ambient air is mixed with a high concentration of ozone so that any NO in the air sample will react and thereby produce light. The light intensity is measured with a photomultiplier and converted into an electronic signal that is proportional to the NO concentration. To measure NO_x concentrations, the sum of NO and NO₂ (nitrogen dioxide), the air sample is first reduced to NO, either by a heated catalyst (molybdenum or gold in the presence of CO) or chemically using FeSO₄, adding to the NO already present in the sample, then into the reaction chamber for measurement as described above. The NO₂ concentration is derived by subtracting the NO from NO_x.

The reduction of NO₂ to NO by these methods is not specific and a number of other nitrogen-containing species are reduced to NO that can interfere with the measurement of NO₂ (e.g., HNO₃, PAN, N₂O₅, HONO, and NO₃). Therefore the thermal catalytic method is used to measure NO, and then NO plus other nitrogen oxides as a group. If the group is not well defined, it is referred commonly as NO_x, since the species included in the group depend on factors such as inlet and line losses and environmental factors. HNO₃ is most prone to line losses. Placing the converter as close to the sample inlet as possible minimizes these losses. Chemiluminescence analyzers that are configured in this manner are commonly known as NOy analyzers. NOy, or reactive nitrogen oxides, consists of a variety of species, the most abundant of which are NO, NO₂, PAN and HNO₃. A TEI 42S NO/NOy analyzer will be used in the mobile van. The instrument has a detection limit of about 0.1 ppb (60 sec averaging times).

4.3.3 Carbon monoxide

The TEI Model 48C carbon analyzer will be used in the mobile sampling. The instrument has a lower detection limit of 0.4 ppb. The analyzer is based on EPA Method EQSA-0486-060.

4.3.4 Automated Gas Chromatography with Mass Spectrometry

The system we propose to use for this project is the unit that is currently being used by DRI in the Central California Ozone Study. The system is based upon a commercial GC/MS system, a commercial preconcentrator/inlet and a custom-built manifold to introduce the sample from outside the shelter to the inlet. The system consists of a Varian 3800 Gas Chromatograph which is interfaced to an Entech model 7100 automated preconcentrator, a Varian Saturn 2000 Ion Trap Mass Spectrometer, and windows-based PC to manage the analytical and data acquisition operations.

The inlet system consists of a pump, two Silicosteel canisters and appropriate valves, flow control and electronic controller. This allows a sample to be collected slowly, integrating the sample over 40 minutes (or longer) and then injecting the sample through the preconcentrator. Two canisters are used so that one can be evacuated and cleaned while the other is filling with the next sample. This way the carryover of compounds from one sample to the next is minimize.

A dual column system is used to measure the full range of C₂ to C₁₂ hydrocarbons. A conventional non-polar capillary column (such as 60 m DB-1) for analytes above C₄ and a porous layer open tubular (PLOT) column is used for C₂ to C₄ analytes. The Al₂O₃/KCl PLOT column provides excellent separation of these important compounds while not requiring cryogenic starting temperatures. The effluent from this column will be sent to a flame ionization detector (FID). This is because these compounds do not require the confirmation of the mass spectrometer.

The target species are listed in an alphabetical order in Table 1 along with their database mnemonic, their carbon number, molecular weight, and some information on known problems encountered during analysis. This list includes C₂ to C₁₂ hydrocarbons, methanol, ethanol, and other alcohols. Also included are C₂ and larger carbonyls including acetone, methyl ethyl ketone (butanone), benzaldehyde and others. MTBE and other oxygenates used in fuels are included as is isobutene, an important breakdown product of MTBE. Oxygenated compounds in surface coatings such as benzaldehyde, benzoic acid, and butylacetate are also included as are the biogenics isoprene, alpha and beta pinene and limonene. Commonly detected halocarbons are also included. The detection limits for these species are about 0.2 ppbv for all targeted species.

4.1.5 Canister Sampling System

Stainless steel SUMMATM-polished canisters of 3-L capacity will be used for volatile hydrocarbon (C₂-C₁₂) collection. These canister samples are suitable for analysis of speciated hydrocarbons by EPA Method TO-14, as well as for analyses of CO, CO₂, methane, and oxygenated species. Prior to sampling, the canisters are cleaned by repeated evacuation and pressurization with humidified zero air, and certified as described below. The sampling

procedure essentially follows the pressurized sampling method described by EPA Methods TO-12 and TO-14 and the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). A stainless steel Viton pump draws in ambient air from the sampling manifold to fill and pressurize the sample canisters. A flow control device maintains a constant flow into the canisters over the desired sample period. This flow rate is preset to fill the canisters to about 1 atm above ambient pressure at the end of the sampling period (as described by EPA Method TO-14).

Prior to sampling, the canisters are cleaned by repeated evacuation and pressurization with humidified zero air, as described in the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215). Six repeatable cycles of evacuation to ~0.5 mm Hg absolute pressure, followed by pressurization with ultra-high-purity (UHP) humid zero air to ~20 psig were used. The differences between the DRI procedure and the EPA recommended method is that in the DRI method canisters are heated to 140 °C during the vacuum cycle, and more cycles of pressure and vacuum are used. At the end of the cleaning procedure, one canister out of six in a lot is filled with humidified UHP zero air and analyzed by the gas chromatograph/flame ionization detection (GC/FID) method. The canisters are considered clean if the total non-methane organic compound (NMOC) concentration is less than 20 ppbC.

4.1.6 Sampling Method for Heavy Hydrocarbon

Heavy hydrocarbons, defined as hydrocarbons in the range of C8 to C20, are collected using Texan-TA (Alltech) solid adsorbent. Prior to use, the Tenax-TA solid adsorbent are cleaned by Soxhlet extraction with hexane/acetone mixture (4/1 v/v) overnight, and dried in a vacuum oven at ~80 °C. The dry Tenax is packed into Pyrex glass tubes (4 mm i.d. x 15 cm long, each tube containing 0.2 g of Tenax) and thermally conditioned for four hours by heating in an oven at 300 °C under nitrogen purge (25 ml/min nitrogen flow). Approximately 10% of the precleaned Tenax cartridges are tested by GC/FID for purity prior to sampling. After cleaning, the Tenax cartridges are capped tightly using clean Swagelok caps (brass) with graphite/vespel ferrules, placed in metal containers with activated charcoal on the bottom, and kept in a clean environment at room temperature until use. When the exposed cartridges are removed, they are immediately plugged with Swagelok caps, and stored in a can designated for exposed cartridges with activated charcoal on the bottom. The exposed cartridges are stored inside a refrigerator and returned to the laboratory in a cooler.

4.1.7 GC/FID Analysis of C2-C12 Hydrocarbons

Gas chromatography with flame ionization detector is the established technique for monitoring volatile hydrocarbons, ozone precursors, in ambient air. The DRI analytical procedure for analysis of C2-C12 hydrocarbons is consistent with the EPA document "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (October 1991, EPA/600-8-91/215) and is described below. Current list of the compounds that are quantified include 160 compounds.

The GC/FID response is calibrated in ppbC, using primary calibration standards traceable to the National Institute of Standards and Technology (NIST) Standard Reference Materials (SRM). The NIST SRM 1805 (254 ppb of benzene in nitrogen) is used for calibrating the analytical system for C₂-C₁₂ hydrocarbon analysis, whereas 1 ppm propane in a nitrogen standard (Scott Specialty Gases), periodically traced to SRM 1805, is used for calibrating the light hydrocarbon analytical system. Based on the uniform carbon response of the FID to hydrocarbons, the response factors determined from these calibration standards are used to convert area counts into concentration units (ppbC) for every peak in the chromatogram.

4.4 Source Composition Profiles and Source Attribution

The emissions inventory is the starting point for a CMB source apportionment to identify potential contributors to ambient concentrations. Vehicle-related emissions, including exhaust, evaporated fuel, and even liquid fuels are ubiquitous in all urban areas and are always included. Architectural (i.e., paints) and industrial solvents (i.e., cleaning and process solvents, as in printing) are also common to, but highly variable in, most urban areas. Petrochemical production and oil refining are more specific to certain urban areas where these facilities exist. Biogenic emissions are larger in the eastern U.S., where forests are lush, in contrast to the arid west.

The source composition profiles that are used in receptor modeling and as input to photochemical air quality models should be current and regionally specific in order to account for temporal and regional variations in fuel formulations and distribution of area and point sources. The major sources for which updated profiles need to be considered for this project are emissions from regional background, motor vehicle exhaust, gasoline liquid and headspace, surface coating, commercial natural gas, liquefied petroleum gas, and industrial facilities. The source samples that are proposed for this project are described in this section along with currently available profiles that may be applicable for this project.

Regional Background and Biogenic Emissions. Regional upwind, background VOC compositions will be derived from ambient samples collected at Catalina Island and San Nicolas Island during the 1997 Southern California Ozone Study (SCOS-NARSTO). These samples typically contain higher abundances of relatively nonreactive hydrocarbons such as ethane and propane and oxidized species, primarily aldehydes.

Vehicle Exhaust. In urban locations, motor vehicle exhaust and evaporative emissions of gasoline are major sources of hydrocarbon emissions. Composites of dynamometer measurements of vehicles of varying age and mileage or on-road measurements (e.g., tunnels and roadways) are commonly used to represent fleet-averaged exhaust profiles. Profiles based on dynamometer tests should include a weighted sum of exhaust profiles for noncatalyst vehicles, high-emitting vehicles and catalyst-equipped vehicles with site-specific weighting factors to approximate the fleet-averaged exhaust composition. The fuels used in the dynamometer tests should resemble the fuels used in the study region at the time the ambient samples are collected. On-road measurements are usually preferred in CMB applications because they include a composite of the exhaust from many vehicles, which more closely represents the local vehicle population than dynamometer tests of a small sample of vehicles. However, tunnel measurements also include varying amounts of diesel exhaust and running evaporative losses.

Diesel and gasoline exhaust profiles are similar with respect to the composition of light hydrocarbons, and are often collinear in CMB calculations. Ethene, acetylene, 1-butene, isobutene, propane, propene, isopentane, n-pentane, 2,2 dimethylbutane, 2-methylpentane, n-hexane, benzene, 3-methylhexane, toluene, ethylbenzene, m- & p-xylene, m-ethyltoluene, and 1,2,4-trimethylbenzene, are the most abundant compounds in either or both of these emissions. Several of these are short-lived, and are only used in CMB calculations where fresh emissions are expected. Major differences between these two exhaust profiles are evident for: 1) acetylene, isobutene, isopentane, n-hexane, and 2-methylhexane, which are most abundant in gasoline exhaust; and 2) for propene, propane, 2,2 dimethylbutane, n-decane, and n-undecane which are more abundant in diesel exhaust. Previous studies showed that source attributions between tailpipe and evaporative emissions from receptor modeling can vary greatly depending on the particular profile chosen for tailpipe emissions (Harley et al., 1992, Fujita et al., 1994, Pierson et al., 1996). This is because tailpipe emissions are a mixture of hydrocarbons produced during combustion (e.g., acetylene, ethene, propene, and benzene) along with unburned gasoline resulting from incomplete combustion. The relative abundances of combustion by-products in the exhaust profile vary with emission control technology, level of vehicle maintenance and operating mode. In the CMB calculation, liquid gasoline represents the additional unburned gasoline (due to misfiring and other engine malfunctions) that is not included in the exhaust profile, plus evaporative emissions from gasoline spillage, hot soaks, and some portion of resting losses (leaks, permeation). The profile for gasoline headspace vapor is taken to represent fuel tank vapor losses (e.g., migration of fuel vapor from the canister).

The reformulation of gasoline has significantly effected the composition of motor-vehicle related emissions in recent years. Both the federal government and the State of California have developed specifications for reformulated gasoline (RFG). The federal program is required for all severe and extreme ozone nonattainment areas, whereas the California program applies throughout the state. Both California and federal RFGs were introduced in two phases. California Phase 1 was introduced in 1992 and Phase 2 was introduced in 1996. Phases I of the federal program was introduced in 1995 and Phase II is scheduled for 2000.

California Phase 1 gasoline had reduced RVP (Reid vapor pressure) in summertime and 2% oxygen (about 11% methyl-tert-butyl ether) in winter. Average specifications for federal Phase I gasoline include RVP of 7.1 psi, 2.0% by weight oxygen content, and 1.0% by weight benzene content. These requirements were effective as of January 1, 1995 in nine major metropolitan areas of the United States with the worst ozone air pollution. The RFG program is federally implemented year-round in these areas as an emission reduction program to control ozone and air toxic emissions. Tertiary amyl methyl ether (TAME), ethyl tertiary butyl ether (ETBE), and ethanol are found in a small percentage of reformulated fuels.

The California Phase 2 RFG specifications apply to all gasoline sold in California beginning January 1, 1996, and include a maximum 80 ppmw sulfur content (average of 30 ppmw), a maximum 1.2% benzene content by volume (average of 0.8), a maximum 10.0% olefin content, a maximum 2.7% oxygen content by volume, a maximum T90 and T50 of 330 °F and 220 °F, respectively, maximum 30% aromatic hydrocarbon content by volume (average of 20%), and a maximum RVP of 7.0 psi. Investigations of the effects of RFG on automotive emissions have been conducted through the Auto/Oil Air Quality Improvement Research Program

(AQIRP), by EPA, ARB, and individual oil companies. Results of the Auto/Oil AQIRP are illustrative of the general response of automotive emissions to changes in fuel parameters.

Compositional differences of vehicle exhaust from Transitional Low Emission Vehicles (TLEVs) operating on conventional industry-average gasoline (RF-A) versus California Phase 2 RFG were summarized by the ARB (1993). The summary includes data from testing programs conducted by the ARB, the Auto/Oil AQIRP, and Chevron Research & Technology Company. The motor vehicle test data were renormalized in terms of weight fractions, and the weight fractions for each species for all tests on an individual vehicle were averaged. The composite profiles for each vehicle were averaged to create composite profiles for each fuel. Separate composite profiles were calculated for each bag of the U.S. EPA 1975 Federal Test Procedure (FTP). For the composite FTP, the average weight fraction of n-alkanes decreased from 15.3% with RF-A to 8.5% with RFG, while the branched alkanes increased from 24.5% with RF-A to 35.8% with RFG. The relative abundances of cycloalkanes and alkynes remained unchanged, while olefins and oxygenates showed slight increases with RFG. Emissions of aromatic compounds decreased from 35.2% with RF-A to 27.7% with RFG. Differences are higher for specific compounds (e.g., benzene and MTBE). These compounds or their ratios serve as useful tracers for RFG.

Gasoline Liquid and Vapor. Running and resting losses are the two sources of evaporative loss from vehicles travelling on the road. Running losses are releases of gasoline vapor from the fuel system during vehicle operation as a result of the heating of the fuel tank. Vapors are released when the rate of fuel vapor formation exceeds the capacity of the vapor storage and purge systems. The composition of running losses tend to resemble headspace vapors if the canister is saturated, and butane-enriched vapors if the canister is not saturated. The canister similarly affects the composition of diurnal evaporative emissions. Resting loss evaporative emissions are due to migration of fuel vapors from the evaporative canister, from leaks, and from fuel permeation through joints, seals, and polymeric components of the fuel system. Most of these losses tend to appear more like whole liquid gasoline. Hot soaks also resemble liquid gasoline.

Liquid gasoline contains many compounds in common with gasoline-vehicle exhaust. It is depleted in products of combustion such as ethane, ethene, acetylene, propene, and to some extent, benzene. Evaporated gasoline is also depleted in these combustion compounds, as well as heavier hydrocarbons that volatilize more slowly from liquid fuels. Isobutane, n-butane, t-2 butene, and especially isopentane are enriched in evaporated gasoline. MTBE and its thermal decomposition product, isobutylene, stands out as a large constituent of gasoline exhaust emissions that clearly separates these from diesel in areas where it is used as an additive. These differences are sufficient for CMB separation of gasoline exhaust from liquid and evaporated gasoline, and often from diesel exhaust, in ambient air.

Commercial Natural Gas and Liquefied Petroleum Gas. The commercial natural gas (CNG) profile is based on samples taken in the summer of 1972 at Los Angeles, CA and in the summer of 1973 at El Monte, CA (Marysohn et al., 1976, 1977). The geogenic natural gas (GNG) profile is based upon samples taken in the spring of 1972 in Newhall, CA and at a well head in Redondo Beach, CA in the fall of 1973. The composition of the samples of both types of natural gas did not vary despite the differences in time and location of sample collection (Fujita

et al., 1994b).

Surface Coatings. Although solvents from paints and industrial uses are large components of all ROG inventories, their reported profiles are few (Guo et al., 1998; Kitto et al., 1997). The most recent data are those of Censullo et al., (1996). Eleven categories of coating were analyzed in this study. In all detailed species profiles were obtained for 106 samples of water-based and solvent-based coating samples. Surface coating profiles for solvent-based industrial maintenance coatings, solvent-based medium gloss/high gloss, solvent-based primers and sealers, quick dry primers and enamels, and thinning solvent were applied in the apportionments. These are largely depleted in the species common to fuel use and production, with larger abundances of styrene, n-decane, and especially “other” compounds. The “other” VOCs are quantified and differ substantially among the different coatings tested. Most of these other compounds are oxygenated compounds that are not measured in PAMS. California and other states requires special solvent and coating formulations to comply with air quality emissions requirements. Coating and solvent profiles are likely to be very specific to a particular area.

Unidentified. Most source profiles used in this study contain a UNID component, which represents the fractional compositions of NMHC that were not assigned to individual, identified species in the gas chromatographic analysis. A single constituent source profile (UNID is taken to constitute 100 percent of NMHC) has been used in the past (Fujita et al., 1994b) to account for the contributions from this component. The difference between the measured total NMHC and the sum of the source contributions from fitted sources is named as “unexplained”. The “unexplained” source contributions in this report refer to the differences between the measured NMHC and the sum of the predicted contributions from those identified source categories. Nearly all of the unexplained mass is related to UNID that is not assigned to the identified categories. The fraction of UNID is consistently higher in downwind and afternoon samples, which suggests that much of this residual UNID could be secondary organic species produced by photochemical reactions.

Table 4-1
PAMS Sites in the South Coast Air Basin

Site	Type of Site	Year Installed	Measurement Method	
			Hydrocarbons	Carbonyl Compounds
Hawthorne	PAMS - 1	1998	Canister/GC-FID ^a	
Burbank	PAMS - 1/2	1998	Auto-GC ^b	DNPH/HPLC ^b
Pico Rivera	PAMS - 2	1994	Auto-GC ^b	DNPH/HPLC ^b
Banning	PAMS - 2	1994	Canister/GC-FID ^a	DNPH/HPLC ^a
Azusa	PAMS - 3	1994	Canister/GC-FID ^a	
Upland	PAMS - 4/1	1994	Canister/GC-FID ^a	
Santa Clarita	PAMS - 3	1999	Canister/GC-FID ^a	

Type 1 - Upwind background.

Type 2 - Maximum precursor emissions (typically located immediately downwind of the central business district).

Type 3 - Maximum ozone concentration.

Type 4 - Extreme downwind transported ozone area that may contribute to overwhelming transport in other areas.

a - Eight 3-hr samples beginning at 00, 03, 06, 09, 12, 15, 18, 21, PST every third day 7/1 to 9/30.

b - Eight 3-hr samples beginning at 00, 03, 06, 09, 12, 15, 18, 21, PST every day 7/1 to 9/30.

Table 4-2
List of PAMS Target Hydrocarbons

1	Ethylene	29	2,3-Dimethylpentane
2	Acetylene	30	3-Methylhexane
3	Ethane	31	2,2,4-Trimethylpentane
4	Propene	32	n-Heptane
5	Propane	33	Methylcyclohexane
6	Isobutane	34	2,3,4-Trimethylpentane
7	1-Butene	35	Toluene
8	n-Butane	36	2-Methylheptane
9	trans-2-Butene	37	3-Methylheptane
10	cis-2-Butene	38	n-Octane
11	Isopentane	39	Ethylbenzene
12	1-Pentene	40	m&p-Xylene
13	n-Pentane	41	Styrene
14	Isoprene	42	o-Xylene
15	trans-2-Pentene	43	n-Nonane
16	cis-2-Pentene	44	Isopropylbenzene
17	2,2-Dimethylbutane	45	n-Propylbenzene
18	Cyclopentane	46	1-ethyl 3-methylbenzene
19	2,3-Dimethylbutane	47	1-ethyl 4-methylbenzene
20	2-Methylpentane	48	1,3,5-Trimethylbenzene
21	3-Methylpentane	49	1-ethyl 2-methylbenzene
22	2-Methyl-1-Pentene	50	1,2,4-Trimethylbenzene
23	n-Hexane	51	n-decane
24	Methylcyclopentane	52	1,2,3-Trimethylbenzene
25	2,4-Dimethylpentane	53	m-diethylbenzene
26	Benzene	54	p-diethylbenzene
27	Cyclohexane	55	n-undecane
28	2-Methylhexane		Total NMOC

Table 4-3
Measurements at Fixed Sites During Field Study

Site	South Coast AQMD					DRI	Others
	O3	NO/NOx	CO	PM10 mass	PAMS		
Hawthorne	x	x	x		canister/GC-FID		
North Long Beach	x	x	x	TEOM			
Lynwood	x	x	x				
Anaheim-Harbor Blvd	x	x	x	BAM			
Burbank-W Palm Avenue	x	x	x	TEOM	auto GC-FID, DNPH		PAN (DGA)
Los Angeles-North Main	x	x	x	BAM	canister/GC-FID (ARB)	Aethalometer	
Pasadena-S Wilson Avenue	x	x	x				
La Habra	x	x	x				
Pico Rivera	x	x	x		auto GC-FID, DNPH		
Azusa	x	x	x	BAM	canister/GC-FID	Auto GC/MS, Aethalometer	PAN (DGA), NOy (CE-CERT)
Pomona	x	x	x				
Upland	x	x		TEOM	canister/GC-FID		
Riverside-Rubidoux	x	x	x	BAM, TEOM			